4 Surface and Material Characterization Techniques

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4.1 Introduction

In the analysis of adhesion bonding, possessing knowledge of the composition and structure of the adherend surface is important. Characterization of bonding surfaces aids both in design and failure analysis of a bond, should the adhesion bond fail.

Surface analysis is the use of microscopic chemical and physical probes that give information about the surface region of a sample. (The term "sample" refers to any piece of material, structure, device, or substance that is under study). The probed region may be the extreme top layer of atoms (the only true surface, for purists), or it may extend up to several microns (millionths of a meter) beneath the sample surface, depending on the technique used. Analysis provides information pertaining to chemical composition, level of trace impurities, and physical structure or appearance of the sampled region. Such information is important to researchers and manufacturers who must understand the materials in order to verify a theory or to create a better product.[1]

Many of the techniques used to probe surfaces utilize a beam of ions (e.g., secondary ion mass spectroscopy, SIMS) to strike the surface and knock atoms off the sample material. These atoms are ionized and identified and measured using a technique known as mass spectrometry. Another technique is ion scattering spectroscopy (ISS), which probes the outermost layer of the surface. If a beam of ions is directed at a sample surface, then a certain number will be elastically reflected. Measurement of the energy of the backscattered particles can be used to identify the mass of these atoms. The intensity of the scattered ions, as a function of angle of emission, provides information regarding the surface crystallographic structure. The variation in the intensity of the scattered beam is partly due to the shadowing of substrate atoms by adsorbed atoms. Using scattering theory, knowledge of the sites that the surface atoms occupy can be derived.[2,3]

Other probes strike the surface with electrons (Auger spectrometry; energy dispersive X-ray spectroscopy, EDS or EDAX) or X-rays (electron spectroscopy for chemical analysis, ESCA or total reflection X-ray fluorescence, TXRF) and measure the resulting electron or photon emissions to probe the sample. Measurements of the way high-energy helium nuclei bounce off a sample can be used as a sensitive measure of surface layer composition and thickness (Rutherford backscattering spectrometry, RBS).

Surface structure on a microscopic scale is observed by using scanning electron microscopy (SEM), optical microscopy, and atomic force or scanning probe microscopy (AFM/SPM).

NOTE: All of these techniques must be performed in a high-vacuum environment—characterized is the substrate under those conditions, not atmospheric conditions under which most bonding processes are done.

Table 4.1 and Fig. 4.1 show a comparison of the sampling depth of traditional methods with those of new techniques. These analyses can focus on a much shallower thickness of the surface, and virtually yield analyses of the outermost layers of a polymer article.

In addition to surface specific methods, a number of other analytic techniques that can be applied to characterize the bulk properties of materials are discussed in this chapter.

4.2 Infrared Spectroscopy

During analysis by infrared spectroscopy (IR), a sample is subjected to electromagnetic radiation in the infrared region of the spectrum. The wavelengths that are absorbed by the sample depend on the nature of the chemical groups present. These wavelengths are defined by a wave number (cm^{-1}) that is obtained by dividing the number 10,000 by the wavelength in microns. The ranges of various wave numbers are given in Table 4.2. Absorbance is defined per Eqn (4.1) and varies from 0 (100% transmission) to infinity (0% transmission). Absorbance is related to concentration of the absorbing species by Beer's law (Eqn (4.1)).

Handbook of Adhesives and Surface Preparation, ed. Sina Ebnesajjad. DOI: 10.1016/B978-1-4377-4461-3.10004-5
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Table 4.1 Comparison of Average Sample Depth for Various Surface Analysis Techniques[4]

Analysis Method	Sampling Depth
Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, conventional secondary ion mass spectroscopy (conventional SIMS)	<2 μm
Energy dispersive X-ray (EDS or EDAX)	<5,000 Å
Rutherford back scattering (RBS)	<400 Å
Surface secondary ion mass spectroscopy (surface SIMS)	<300 Å
Electron spectroscopy for chemical analysis (ESCA) also called X-ray photoelectron microscopy (XPS)	<100 Å
Auger electron spectroscopy (AES)	<100 Å
Ion scattering spectroscopy (ISS), also called low-energy ion scattering (LEIS)	<2 Å
Time-of-flight secondary ion mass spectroscopy (TOF-SIMS)	1.3 Monolayers
Atomic force microscopy (AFM) or scanning probe microscopy (SPM)	0.1 Å

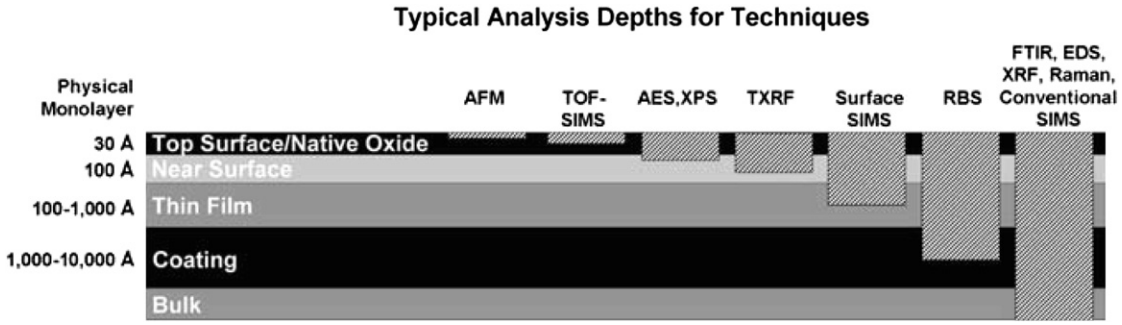

Figure 4.1 Sampling depth for surface analysis techniques.[1]

Table 4.2 Definition of Electromagnetic Wave Ranges

Definition of Range	Wave Number (10^4 cm^{-1})	Wave Length (μm)
Ultraviolet	5–2.5	0.2–0.4
Visible	2.5–1.42	0.4–0.7
Near IR	1.42–0.4	0.7–2.5
IR	0.4–0.02	2.5–50
Far IR	0.02–0.0012	50–830

$$\text{Absorbance} = \text{Log}\frac{100}{\%\ \text{Transmission}} \tag{4.1}$$

$$\text{Absorbance} = Kcl \tag{4.2}$$

K = a constant that is occasionally called the *extinction coefficient,*

c = concentration of the absorbing species, and

l = sample thickness

Equation (4.2) can be used to determine the concentration of a compound in a solution, if the value of K is known for that compound. Chemical bonds such as C–O, O–H, and so on, absorb different amounts of infrared energy over various wavelengths. Absorption patterns vary from sharp to broad for different bonds. Peak IR absorption wavelength (wave number) is characteristic of a chemical bond. Absorption over the infrared *spectrum* is a fingerprint characteristic of an organic material. Qualitative identification can be achieved by obtaining and analyzing the IR spectrum of a material.

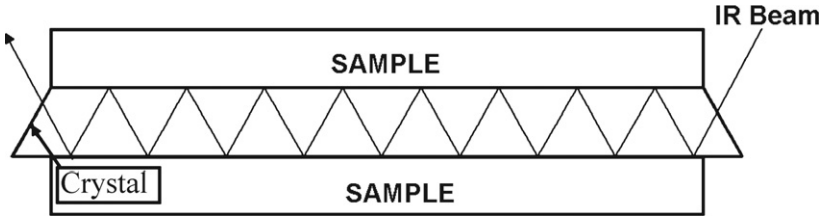

Figure 4.2 Schematic of the sample configuration relative to the reflective crystal in attenuated total reflectance IR.

Infrared spectra can also be obtained by reflecting the IR beam on the surface of a sample. This technique is applied when obtaining an IR spectrum by a transmission technique is not possible. Attenuated total reflectance (ATR), also known as ATIR (attenuated total internal reflectance), is based on multiple internal reflectances of the IR beam on the sample surface using a high refractive index crystal (e.g., thallium bromo-iodide). The IR beam is entered into the crystal at an angle, and after about 25 internal reflections (5 cm), a spectrum similar to that of the transmission is obtained. The sample is in tight contact with both surfaces on the crystal, as seen in Fig. 4.2.

Modern infrared spectrometers use Fourier transform for the calculation of results. The method is called Fourier transform infrared spectroscopy, abbreviated as *FTIR*.

4.3 Raman Spectroscopy

When incident light strikes a sample, part of the light is scattered. Most of the scattered light has the same wavelength as the incident light; this is called Rayleigh scattering. Some of the light is scattered at a different wavelength; this is called Raman scattering. The energy difference between the incident light and the Raman scattered light is called the Raman shift. It is equal to the energy required to vibrate or rotate the molecule. Several different Raman shifted signals will often be observed in a single sample; each is associated with different vibrational or rotational motions of molecules in the sample. The particular molecule and its environment will determine what Raman signals are observed. In practice, because the Raman effect is so slight, a laser is used as the source of the incident light. A plot of Raman intensity versus the frequency of the Raman shift is a Raman spectrum. It usually contains sharp bands that are characteristic of the functional groups of the compounds or materials. This information can be interpreted to determine chemical structure and to identify the compounds present. It is complementary to FTIR in that it uses a different method to measure molecular vibrations.

Raman spectroscopy is a good technique for qualitative analysis and discrimination of organic and/or inorganic compounds in mixed materials. A Raman spectrum can be obtained from samples that are as small as 1 μm.[1] The intensities of bands in a Raman spectrum depend on the sensitivity of the specific vibrations to the Raman effect and are proportional to concentration. Thus, Raman spectra can be used for semiquantitative and quantitative analyses. The technique is used for identification of organic molecules, polymers, biomolecules, and inorganic compounds both in bulk and as individual particles. Raman spectroscopy is particularly useful in determining the structure of different types of carbon (diamond, graphitic, diamond-like-carbon, etc.) and their relative concentrations.

4.4 Scanning Electron Microscopy (SEM)

SEM is a useful technique for the analysis of plastics surfaces. Actually, it is useful for any surface that survives in a vacuum. Almost all SEMs start by sputtering the surface with a thin layer of gold metal. If it is not already conductive, this makes the surface conductive, which is a requirement; so, you are often not looking directly at the surface. It involves a finely collimated beam of electrons that sweeps across the surface of the analysis specimen. The beam is focused into a small probe that scans across the surface of a specimen. The beam interactions with the material result in the emission of electrons and photons as the electrons penetrate the surface. The emitted particles are collected with the appropriate detector to yield information about the surface. The final product of the electron beam collision with the surface topology of the sample is an image (Fig. 4.4).

For example, Fig. 4.4 shows the result of topical SEM analysis of a drug-infused polymer coating on

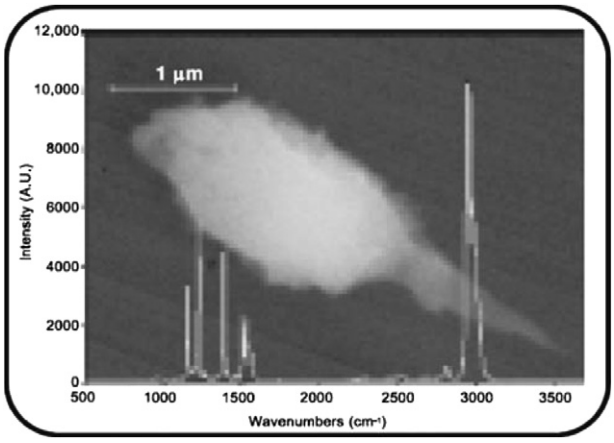

Figure 4.3 Raman spectroscopy identified this micron-sized particle as polyethylene.

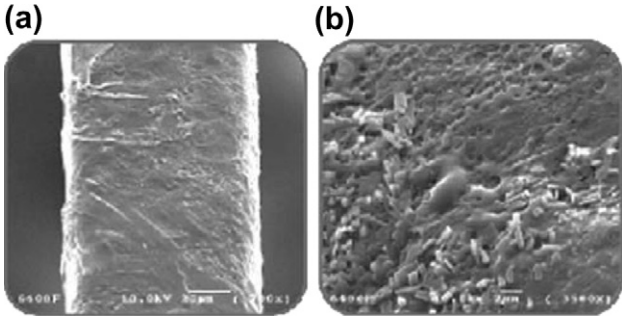

Figure 4.4 SEM images of a polymer-coated device: (*a*) 750 times magnification and (*b*) 35,000 times magnification.[1]

a stainless steel device. SEM of the surface at 750 times magnification is shown in Fig. 4.4(a) and at 35,000 times magnification in Fig. 4.4(b). The higher magnification revealed the presence of crystals on the surface of the coating.

A helpful attachment to the SEM is the *electron microprobe*. An electron beam is focused on a sample surface, causing ionization to a depth of a few micrometers. Energies and wavelength of the emitted X-ray during the de-excitation cycle are characteristic of the elements present in the top layers of the sample. The result is not a true surface analysis, but the electron microprobe allows analysis of various spots of the sample surface.[5]

4.4.1 Environmental Scanning Electron Microscopy (ESEM)

The first commercial environmental scanning electron microscopy (ESEM) was introduced in 1988. Although it is extremely expensive to modify a standard scanning electron microscope (SEM) to perform as an ESEM, a microscope designed for dual function (ESEM/SEM) can operate well in both modes.[6]

One advantage of using the environmental scanning electron microscope (ESEM) is that by operating it in "wet mode" the need to make nonconductive material conductive is eliminated. Material samples do not need to be desiccated and coated with carbon or gold—palladium and thus their original characteristics can be preserved for further testing or manipulation. One may image the sample, modify the sample, and image the sample again, ad infinitum, without destroying its usefulness by having coated it to make it conductive.

Dynamic experiments can also be performed with the ESEM in the wet mode; one of the hot stages may be used to heat a small sample to as high as 1500 °C and image it during every step of the heating/cooling process. After a certain temperature is passed, above 1100 °C, bias actually needs to be adjusted to reject thermal electrons, but this can be done easily.

The Peltier heating/cooling stage[7] allows working within 20 °C above or below ambient temperature, and the combination of low temperature (e.g., 4 °C) and high water vapor pressure (e.g., 6.1 Torr) permits achievement of 100% relative humidity (RH) at the sample surface. At 100% RH, samples are not dehydrated during the imaging process. At less than 100% RH, a moist sample constantly loses water as the vacuum in the chamber pumps on it; in the "scope," it appears as constant movement of the sample.

4.5 Rutherford Backscattering Theory

RBS is based on collisions between atomic nuclei and derives its name from *Lord Ernest Rutherford*, who in 1911 was the first to present the concept of nuclei in atoms. It involves measuring the number and energy of ions in a beam, which backscatter after colliding with atoms in the near-surface region of a sample where the beam has been targeted. With this information, determining atomic mass and elemental concentrations versus depth below the surface is possible. RBS is ideally suited for determining the concentration of trace elements heavier than major

constituents of the substrate. Its sensitivity for light masses, and for the makeup of samples well below the surface, is poor.

When a sample is bombarded with a beam of high-energy particles, the vast majority of particles are implanted into the material and do not escape. This is because the diameter of an atomic nucleus is on the order of 1e-15 m, whereas the spacing between nuclei is on the order of 2e-10 m. A small fraction of the incident particles undergo a direct collision with a nucleus of one of the atoms in the upper few micrometers of the sample. This "collision" does not actually involve direct contact between the projectile ion and target atom. Energy exchange occurs because of Coulombic forces between nuclei in close proximity to each other. However, using classical physics, the interaction can be modeled accurately as an elastic collision.

The energy measured for a particle backscattering at a given angle depends upon two processes. Particles lose energy while they pass through the sample, both before and after a collision. The amount of energy lost is dependent on that material's stopping power. A particle also loses energy as the result of the collision. The ratio of the energy of the projectile before and after collision is called the kinematic factor.

The numbers of backscattering events that occur from a given element in a sample depend upon two factors: the concentration of the element and the effective size of its nucleus. The probability that a material will cause a collision is called its scattering cross section.

4.6 Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is a standard method for identifying and quantifying elemental compositions in a very small sample of even a few cubic micrometers. In a properly equipped SEM, the atoms on the surface are excited by the electron beam, thus emitting specific wavelengths of X-rays that are characteristic of the atomic structure of the elements. An energy dispersive detector, a solid-state device that discriminates among X-ray energies analyzes the X-ray emissions. Appropriate elements are assigned, thus yielding the composition of the atoms on the specimen surface. This procedure is called energy dispersive X-ray spectroscopy, or EDS, and is useful for analyzing the composition of the surface of a specimen (Figs 4.5 and 4.6).

4.7 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is similar to SEM, except for the fact that the beam passes

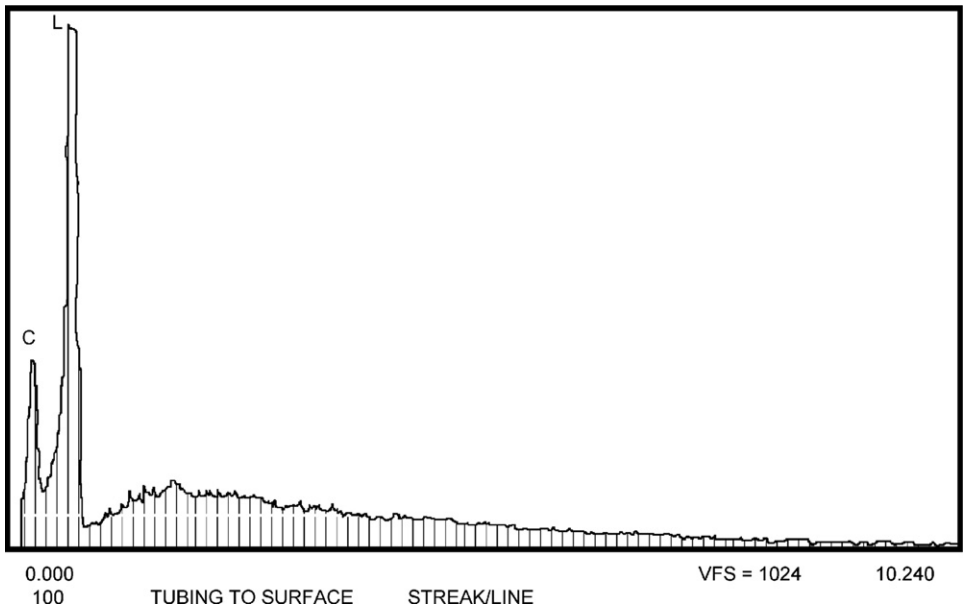

Figure 4.5 EDS elemental analysis of a clean PTFE surface.
(Courtesy of DuPont Fluoroproducts.)

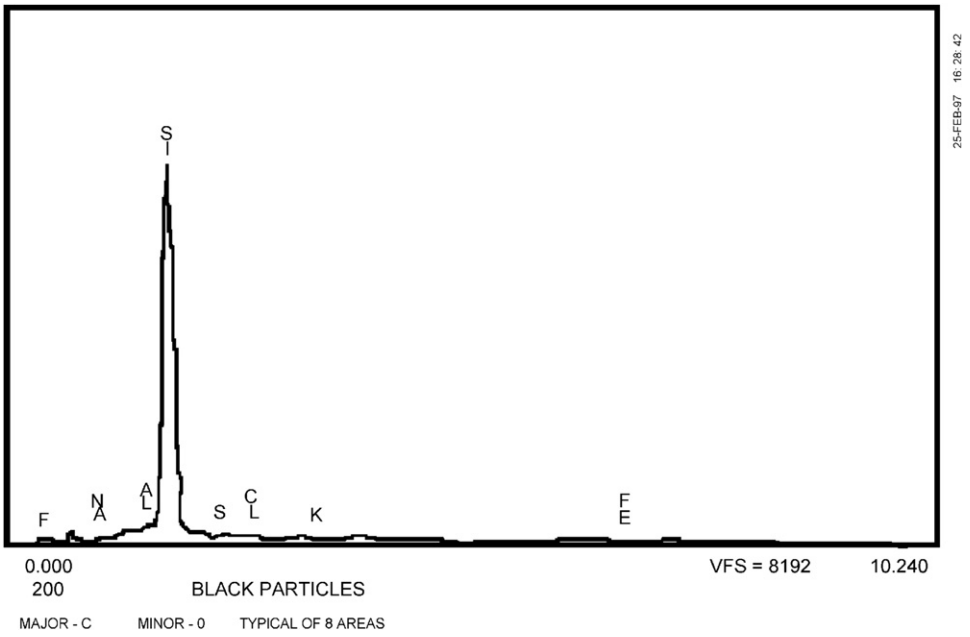

Figure 4.6 EDS elemental analysis of a contamination spot on the PTFE surface. *(Courtesy of DuPont Fluoroproducts.)*

through the sample. A high voltage (80−200 keV), highly focused electron beam is passed through a thin solid sample, typically 100−200 nm in thickness. Electrons undergo coherent scattering or diffraction from lattice planes in the crystalline phase of materials, thus yielding phase identification. Characteristic X-rays that are generated can be detected in a separate detector, permitting qualitative elemental analysis.

Figure 4.7 shows a TEM micrograph of particles of polyvinylidene fluoride that have been produced by emulsion-polymerization in an aqueous phase. Figure 4.8 shows the capability of TEM in revealing the structure of a material. The authors have used nonaqueous miniemulsions to perform polymerizations. Polyvinylpyrrolidone nanoparticles (Fig. 4.8) can be synthesized at temperatures higher than 150 °C in nonaqueous inverse miniemulsions and in the presence of an additional stabilizer. Particle size

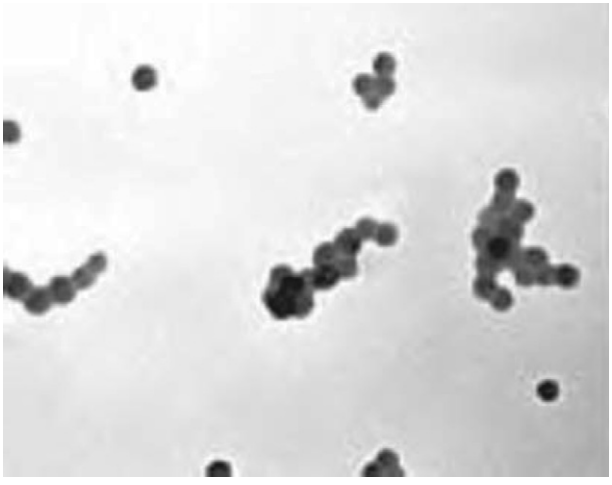

Figure 4.7 Transmission electron micrograph of particles of emulsion-polymerized PVDF particles ($D_p = 128$ nm).[6]

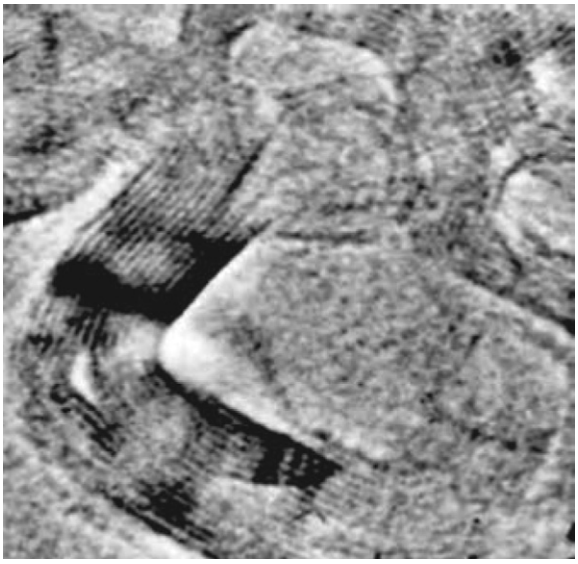

Figure 4.8 TEM micrograph of polyvinylpyrrolidone particles.

and size distribution can be measured from the micrograph because of its excellent resolution.[8]

4.8 Electron Spectroscopy for Chemical Analysis (ESCA)

This is a widely used analytic technique for characterizing polymer surfaces. ESCA is also called X-ray photoelectron spectroscopy (XPS) and is able to detect all elements except hydrogen. A sample is irradiated by X-ray beams, which interact with the inner electron shell of atoms. Photon energy of the X-ray is transferred to an electron in the inner shell, enabling it (*photoelectron*) to escape from the sample surface. An analyzer measures the kinetic energy of the photoelectron, which is equal to the binding energy of this electron. Knowledge of the binding energy allows identification of the element. The chemical bond of an atom to other elements shifts the bonding energy of the photoelectron to higher or lower values. This shift in binding energy provides structural information for a molecule.

Operation and maintenance of ESCA equipment and interpretation of its data are quite complex. Samples intended for ESCA and other surface analysis must be handled carefully because minute contamination can mask the surface structure of the samples. To alleviate this type of complication, the sample surface can be washed with volatile solvents such as methanol, acetone, hydrocarbons, and fluorocarbons using an ultrasound bath. Typically, analysis is conducted before and after the surface wash while studying a sample that has been handled and/or contaminated. Another application of surface wash is removal of loose material that may be weakly bound to the surface. The working details and data interpretation for ESCA are outside the scope of the present book. The interested reader is encouraged to refer to other sources to gain an in-depth understanding of ESCA.[4,9–13]

A typical spectrum of ESCA shows peaks as a function of binding energy, as shown in Fig. 4.9 for polytetrafluoroethylene. C1s and F1s peaks on a "clean" surface indicate that the PTFE surface is comprised of only carbon and fluorine. The energy shift can be curve-fitted by trial and error to determine the functional groups on the surface. The most simplified report that ESCA generates is a survey of the atomic composition of the surface elements, with the exception of hydrogen. A helpful tool to investigate surface changes of a polymer is the ratio of other elements to carbon, as shown in Table 4.3, for the effect of sodium etching on the surface composition of a few different fluoropolymers.

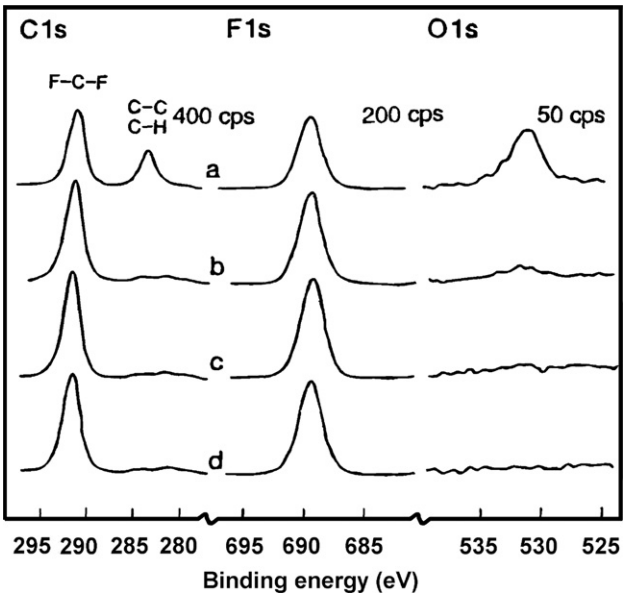

Figure 4.9 XPS spectra of polytetrafluoroethylene (*a*) before cleaning and after cleaning with an ultrasonic cleaner in (*b*) methanol, (*c*) acetone, and (*d*) *n*-heptane.[13]

4.9 Auger Electron Spectroscopy (AES)

Auger refers to the mission of a secondary electron after the surface of a solid has been bombarded with electrons. This is a different phenomenon from photoelectron emission (the basis of ESCA), which occurs after bombardment of a solid surface with low-energy X-rays.[15] The energy of the Auger electron depends on the chemical bonding state of the element from which it has emitted. The depth of the escape of an Auger electron is less than 1 nm, with metals having shortest escape depth and organic material the deepest. Lateral resolution of AES is around 1 μm. Auger spectroscopy, thus, characterizes the surface of materials.

This method uses a low-energy electron gun, with a power less than 5 keV, to lessen the heating and decomposition of the surface. The number of electrons and their energies are detected by a counter and energy analyzer. The energy of the electron identifies the element, whereas the number of emitted electrons indicates the surface concentration of the element.

Table 4.3 Effect of Sodium Etching on the Surface Composition and Adhesion Bond Strength of Fluoropolymers[14]

Polymer	Treatment	Surface Chemical Analysis (%) by ESCA						
		F/C Ratio	Cl/C Ratio	O/C Ratio	Cl	C	F	O
PTFE	–	1.60	–	–	–	38.4	61.6	–
PTFE	Tetra-Etch®[1] (1 min)	0.011	–	0.20	–	82.2	0.9	16.9
PTFE	N/1 min[2]	0.005	–	0.14	–	87.2	0.4	12.4
PVF	–	0.42	–	–	–	70.4	29.6	–
PVF	Tetra-Etch®[1] (30 min)	0.21	–	0.026	–	80.7	17.2	2.1
ECTFE	–	0.64	0.27	–	14.1	52.5	33.4	–
ECTFE	Tetra-Etch®[1] (1 min)	0.16	0.05	0.12	3.8	74.9	12.2	9.1

[1] *Supplied by WL Gore Corporation.*
[2] *Treatment with 1 mole solution naphthalenide in tetrahydrofuran at room temperature.*

4.10 Ion Scattering Spectroscopy (ISS)

When a beam of ions hits a solid surface, part of the projectiles will be scattered back into the vacuum after one or more collisions with target atoms of the top few layers.[16] Measurement of the energy of the backscattered particles can be used to identify the mass of these atoms. The technique is called ion scattering spectroscopy (ISS). The term encompasses several techniques, depending on the energy of the primary ion beam. LEIS (low energy ion scattering) spectroscopy refers to primary energies in the range of 100 eV−10 keV, medium energy ion scattering (MEIS) to a range from 100 to 200 keV, and high energy ion scattering (HEIS) to energies between 1 and several MeV. Often the LEIS technique is called ion scattering spectroscopy (ISS); the term we will use below means LEIS, while HEIS technique is best known as *Rutherford backscattering spectroscopy* (RBS).

LEIS is attractive as a surface-specific technique. Spectra are usually obtained using noble gas ion beams from 0.5 to 3 keV.[17] Due to strong electron affinity of inert-gas ions, the probability of electron transfer is very high, even in the initial collision with a surface atom. After two or more collisions, most ions are neutralized so that a detector set to analyze only ions of the same type as those in the incident beam detects ions that have almost entirely had only one collision with a target atom. Projectiles entering the solid are discarded because they require several scattering events to return to the surface and exit.

The practical use of IIS is determined by its extreme sensitivity to only the top surface layer (for standard experimental arrangements) or two monolayers (for grazing incidence). Typical applications include composition of catalytic surfaces, thin film coatings, and adhesion, as well as arrangement of surface atoms, including the localization of adsorbed atoms. Quantification of surface analysis, using low-energy ions, is hampered by the uncertainty of the inelastic losses and the neutralization rate, depending on ion trajectories. In addition, overlapping peaks and multiple scattering have to be considered, and here computer simulation becomes an indispensable tool.

4.11 Secondary Ion Mass Spectroscopy (SIMS)

This is a valuable technique for identifying the structure and composition of polymer surfaces, and it complements ESCA. ESCA spectra for similar materials are difficult to resolve, whereas SIMS can differentiate among different polymers. This is partly due to the smaller sampling depth required by SIMS. In a typical analysis, the surface of the polymer sample is bombarded by a primary ion at low current density, principally intended to minimize alteration of the sample surface because of irradiation. The polymer surface generates positive and negative ions, which are analyzed using a mass analyzer. The results of detailed analysis provide chemical structure and composition data about the surface. A traditional shortcoming of SIMS, however, is its inability to perform quantitative analysis.

A different type of analyzer called *time of flight* (TOF-SIMS) can be utilized to determine the structure of the sample as a function of sampling depth. TOF-SIMS is used to measure the mass of an ion, so it is a mass analyzer. It can be useful in determining stratification of resins in coatings or diffusion of atoms into an area underneath a surface.[18,19,19A] TOF-SIMS works best for samples that do not degrade by exposure to ion irradiation, such as inorganic material.

Quantitative analysis of organic materials by TOF-SIMS is intrinsically difficult because of their tendency to decompose under ion irradiation. Techniques have, however, been devised to circumvent radiation-induced degradation. In a study, principal component analysis (PCA) was applied as a means of compensation for the spectral degradation caused by this decomposition and this improved the accuracy of the quantitative analysis.[20]

Two organic additives were used that had quite different composition and vulnerability to decomposition under ion irradiation in polystyrene. This enabled the extraction of a principal component related to their content that is independent of the decomposition. It proved the effectiveness of the approach in quantitative analysis of organic additives content in polymers without loss in accuracy due to spectral degradation.

4.12 Mass Spectroscopy (MS) or spectrometry

MS is applicable to both organic and inorganic substances. It is a quantitative technique that allows the study of the structure of organic matter. A sample is degraded, often bombarded with electrons, into fragments that are identified through fractional mass differences in atoms of the same principal mass number.[21] There are two types of mass analyses: one is high resolution that differentiates between fractional mass differences and the second is mass analysis that only differentiates principal mass number. The latter is more common. The method requires extremely low pressure (high vacuum), and the fragments must be volatile. Charged fragments are ejected into vacuum; strictly speaking, this does not mean that they are volatile (implies evaporation). The determination relies on the pattern of fragmentation of a molecule upon ionization. These patterns are distinct, can be reproduced, and are additive for mixtures. A mass spectrum is a graph that shows the measured values of ion intensities per unit charge (*m*/*e*, mass divided by charge). Mass spectrum is unique for each compound (Fig. 4.10). In a high-resolution spectrum, the deviation of the molecular weight of each fragment from an integral value is used to determine the elemental composition.

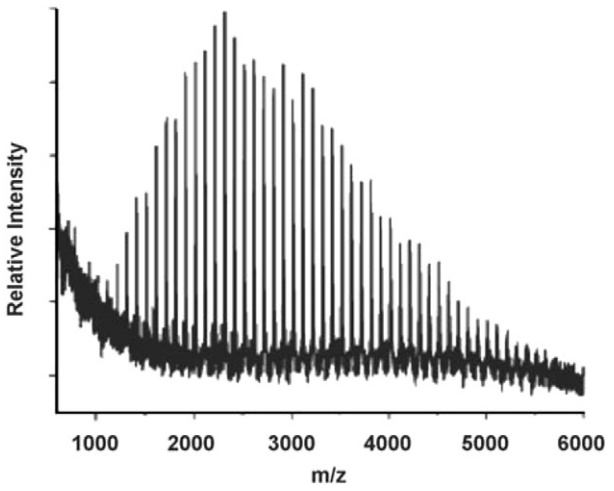

Figure 4.10 Matrix-assisted laser description ionized time-of-flight (MALDITOF) mass spectrum of poly (methylmethacrylate) (PMMA).[22,24]

There are several methods for ionization of organic compounds including particle bombardment, chemical and field ionization, electron impact, field desorption, and laser pulse. For example, in laser micromass analysis methods, a laser pulse is used to supply the necessary energy to volatilize a sample from the surface for mass spectroscopy.[22] Mass spectrometry is often used in conjunction with gas chromatography to identify the separated components. The working technology of mass spectrometry is quite complex.[23]

4.13 Gas Chromatography (GC)

Chromatography separates a mixture into its components, which are then analyzed by one of many detectors. In GC, the sample is passed during the vapor phase through an appropriated solid bed placed in a column. An oven supplies heat to the column, through which the vapor is carried using a constant stream of a gas such as nitrogen or helium. The time required to elute each component (*retention* time) is monitored. (Analysis times can run for more than an hour.) GC refers to the use of solid absorbent or molecular sieve columns. In the majority of GC

columns, the packing is coated with a stationary liquid phase. Separation takes place by partitioning between the liquid coating and the carrier gas.

There are a variety of column packing material and liquid phases. Sometimes a very long capillary column is used without a solid packing and is only coated with a liquid on the wall. The oven can be operated isothermally at a given temperature or according to a program where temperature varies as a function of time.

There are different types of detectors, including thermal conductivity and electron capture types. The most common detector is the *flame ionization* variety (FID). A hydrogen flame is utilized to combust the column effluents. Thermal conductivity detectors do not degrade the effluents and are not as sensitive as flame ionization detectors. Electron capture detection is especially sensitive to halogenated compounds.

Retention time of a compound is a characteristic of that compound under a set of conditions. To resolve an overlap of retention time, a combination of GC with MS or IR is employed. Figures 4.11 and 4.12 show examples of GC/MS spectra for two isomers. Note the similarity that is typical of the GC/MS spectra of various isomers.

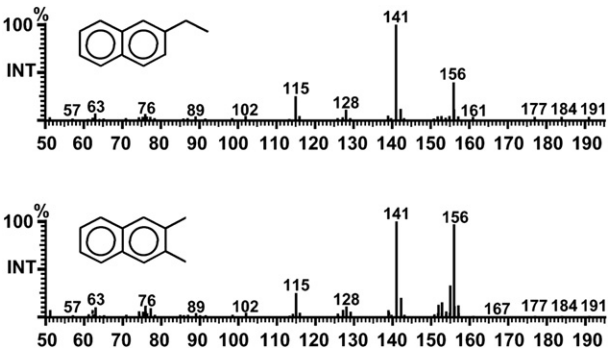

Figure 4.11 GC/MS spectra of alkylated polycyclic aromatic hydrocarbon (PAH) isomers.[23]

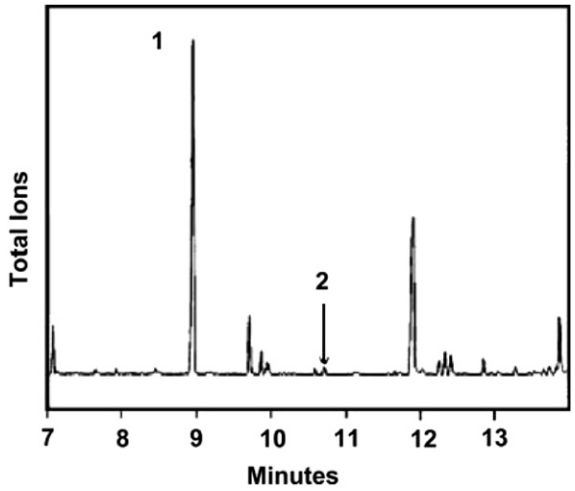

Figure 4.12 GC/MS thermal desorption chromatogram of silicon oil causing poor adhesion of thermally bonded package; peak 1: octamethylcyclotetrasiloxane, peak 2: decamethylcyclopentasiloxane.

4.14 Nuclear Magnetic Resonance (NMR)

NMR is a unique technique that depends on the magnetic nature of a few isotopic nuclei, primarily ^{1}H, ^{13}C, ^{19}F and ^{31}P. In a strong magnetic field, a nucleus processes about the direction of the magnetic field with a frequency proportional to the field strength. A nucleus is bombarded with radio frequency electromagnetic waves at right angles to the magnetic field. When the spinning nucleus and the radio frequency become equal, resonance happens. The energy transfer is the basis of the NMR spectrum of the nucleus and is measured and depicted as a band. The resonance frequency at which the energy absorption occurs depends on the chemical nature of the sample and the environment (e.g., solvent). The nature of the bonds in a molecule can be identified by NMR (Fig. 4.13), by the use of reference spectra and characteristic frequencies for different types of chemical bonds.

If a strong magnetic field is applied to the nuclei, a difference can be found between alignment in the direction of the applied magnetic field and alignment in the opposite direction of the applied magnetic field. In NMR, the constraint that leads to quantized transitions is applied by the spectrometer. Due to this, the frequency of absorption varies with the applied magnetic field and thus there is no absolute frequency or wavelength for a given absorption. NMR spectra are not plotted as absorption versus wave number, as IR spectra are, but are plotted as absorption versus *chemical shift*, d. The chemical shift for proton NMR is the difference between the frequency of absorption of the sample and a standard, tetramethylsilane (TMS), normalized by the frequency of absorption of TMS, which is expressed in parts per million (ppm). Therefore, the above equation is multiplied by 10^{6}.[25]

In IR we consider two states for a bond: vibrating and nonvibrating. The transition associated with the

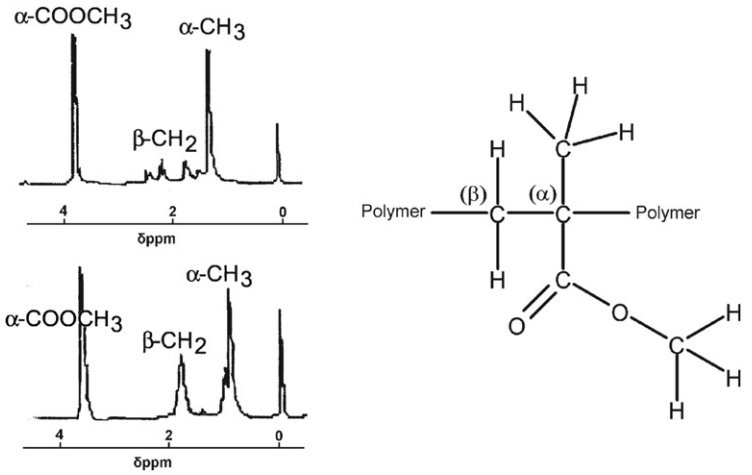

Figure 4.13 Example of NMR frequency shift in elucidating chemical structure of a polymethyl methacrylate.

change from nonvibrating to vibrating leads to the absorption at fixed wave numbers. In NMR several states are possible depending on the spin quantum number. The permitted states are given by the allowable values for the magnetic quantum number, $mI = I, \mathrm{I} - 1, \ldots -I$. For $I = 1/2$ there are two states possible, $mI = 1/2$ and $mI = -1/2$. For $I = 1$ three states are possible, $mI = 1, 0, -1$. For protons the two allowable states are generally spoken of as parallel and antiparallel to the applied field.

PMMA was one of the first polymers studied in depth for tacticity, using proton NMR. For syndiotactic PMMA (bottom), three main absorptions are observed, α-CH_3 at 0.91, β-CH_2 at 1.9, and α-$COOCH_3$ at 3.6. For the isotactic polymer (top curve), the α-CH_3 is more deshielded at 1.20, the β-CH_2 becomes a quartet centered at 1.9 and the α-$COOCH_3$ remains a singlet at 3.6. The splittings of the β-CH_2 in what should be a sequence of 1:1:1:1 is due to two types of methylene groups, termed erythro, e (more deshielded), and threo, t (less deshielded), corresponding to the bottom and top protons in the molecular sketch above. Each of these peaks are split into two peaks by the other, leading to an expected splitting of four equal peaks, with a reported *J* coupling constant of about 0.2 ppm. The e and t protons are separated by 0.7 ppm, which can be verified by molecular modeling. A higher resolution NMR can resolve higher order stereosequences, as shown below for isotactic and atactic PMMA. You should compare the information content of the 60 MHz spectrum above to the 500 MHz spectra below. (Again, 60 MHz refers to the natural resonance frequency of a proton for a given magnetic field of the instrument, ν a B_0.)[26]

4.15 Differential Scanning Calorimetry (DSC)

DSC is one of the best known techniques among a group called *thermal analysis* methods. Others include *differential thermal analysis*, *dynamic mechanical analysis*, and *thermogravimetric analysis* methods; all will be covered in the following sections.

DSC is a thermal analysis technique that is used to measure the heat flows related to transitions in materials, as a function of time and temperature.[28] These measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. Any event, such as loss of solvent, phase transitions, crystallization temperature, melting point, and degradation temperature of the plastic sample, results in a change in the temperature of the sample. The available DSC systems have a wide range of temperature capability, from −60 °C to >1500 °C.

Two types of systems are commonly used: *power compensation* and *heat flux* DSCs. In the former apparatus, temperatures of the sample and the reference are controlled independently by using separate but identical furnaces. The power input to the two furnaces is adjusted to equalize the temperatures. The energy required for the temperature equalization is a measure of the enthalpy or heat capacity of the sample relative to the reference. In *heat flux* DSC, the

sample and the reference are interconnected by a metal disk that acts as a low-resistance heat-flow path. The entire assembly is placed inside a furnace. Changes in the enthalpy or heat capacity of the sample cause a difference in its temperature in relation to the reference. The resulting heat flow is small due to the thermal contact between the sample and the reference. Calibration experiments are conducted to correlate enthalpy changes with temperature differences. In both cases, enthalpy changes are expressed in units of energy per unit mass.

A typical DSC is run isothermally, or with the temperature change at a constant rate under an atmosphere of air, or another gas. In the isothermal case, the heat flow or enthalpy change is plotted against time. In the latter case, heat flow or enthalpy is plotted against temperature or time. Figure 4.14 shows an example of an enthalpy peak generated by an exothermic event or an endothermic event such as melting of the crystalline phase of a semicrystalline or crystalline polymer. Heat of fusion (H_{f0}) represents the enthalpy change at the crystal melting point of T_0. The weight fraction of the crystalline phase (W) can be determined by comparing the measured heat with H_{f0}. A sample of the polymer is heated in a DSC from a temperature of T_1 to T_2, where the polymer becomes amorphous at a temperature of T_0 prior to reaching T_2, as shown by the baseline shift in Fig. 4.14. The enthalpy changes are determined according to the following procedure.

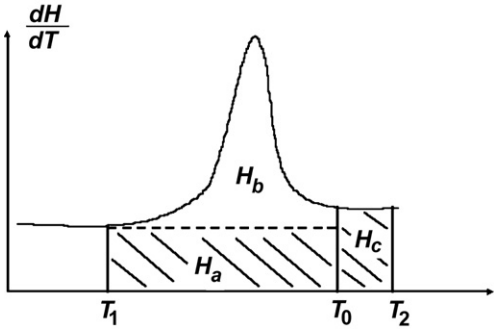

Figure 4.14 Example of a DSC peak.

H_a represents the simple enthalpy change during the heating of the polymer sample from T_1 to T_0. At T_0, the crystalline phase melts and becomes amorphous. The enthalpy of fusion is expressed in Eqn (4.3). The increase in the enthalpy of the amorphous phase as a result of heating from T_0 to T_2 is designated as H_c. If the enthalpy change, calculated from the separation of the DSC curve from the baseline (i.e., area under the curve), is designated as H_T, then Eqn (4.4) can be derived to calculate the weight fraction of the crystalline phase.

$$H_b = WH_{f0} \tag{4.3}$$

$$\begin{aligned} H_T &= H_a + H_b + H_c \\ H_T &= H_a + WH_{f0} + H_c \\ W &= \frac{(H_T - H_a - H_c)}{H_{f0}} \end{aligned} \tag{4.4}$$

An example of a DSC thermogram for two types of polyether ether ketone is given in Fig. 4.15.

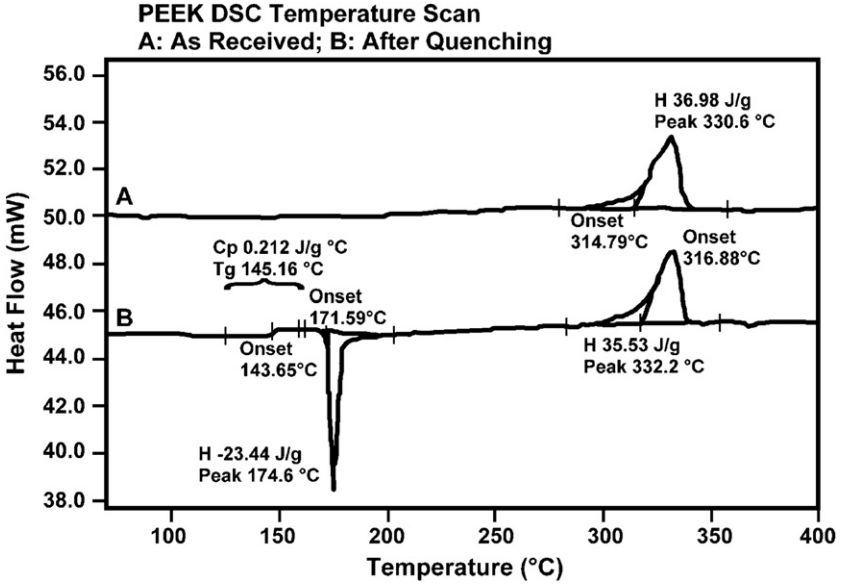

Figure 4.15 DSC thermogram for two types of polyetheretherketone.[27]

4.16 Differential Thermal Analysis (DTA)

This technique measures the temperature difference between a sample and a reference, as temperature is increased. A plot of the temperature difference (thermogram) reveals exothermic and endothermic reactions that may occur in the sample. Temperature for thermal events, such as phase transitions, melting points, crystallization temperatures, and others, can be determined by this method. Maximum temperature capability of DTA is in excess of 1000 °C under air or other gas atmospheres. A typical heat-up rate for DTA is in the range of 10−20 °C/min, although slower rates are possible by using a typical optimum sample weight of 50−100 mg. The sample should be ground to particles finer than 100 mesh.

Melting of a semicrystalline or crystalline polymer manifests itself as an endothermic peak. The peak temperature is correspondent to the actual melting point of the polymer. As in DSC, the area under the peak is proportional to the crystalline fraction of the sample. Mixtures of polymers can be characterized by DTA because the melting points of individual polymers are for the most part unaffected by the mixture. Similar polymers, such as high and low density, are distinguishable by DTA, whereas IR would not be able to easily resolve such subtle differences. Figure 4.16 shows the thermogram of a mixture of polytetrafluoroethylene (PTFE) and perfluoroalkoxy polymer (PFA). Three peaks are noticed: one at about room temperature (19 °C), which is a transition point for PTFE, and two melting points. PTFE and PFA are distinguished by the difference in their melting points.

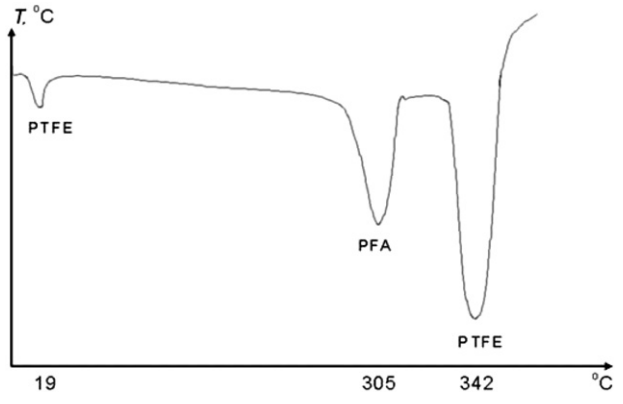

Figure 4.16 Examples of DTA thermogram for PFA and PTFE.

4.17 Dynamic Mechanical Analysis (DMA)

DMA method is generally a more sensitive technique for detecting transitions than are the DSC and DTA methods. This is because the properties measured are the dynamic modulus and damping coefficient, both of which change significantly when crystalline structure transitions to the amorphous phase. The operating principle is that in these transitions, a proportionally larger change occurs in the mechanical properties of a polymer than the change which occurs in its specific heat. DMA is, thus, the preferred method of measurement for glass transition temperature and other minor phase/structure changes of polymers.

The DMA method determines[29] elastic modulus (or storage modulus, G'), viscous modulus (or loss modulus, G''), and damping coefficient (Tan Δ) as a function of temperature, frequency, or time. Results are usually in the form of a graphical plot of G', G'', and Tan Δ as a function of temperature or strain. DMA may also be used for quality control and product development purposes.

The forced nonresonance technique is one of the simpler DMA methods.[30] In the majority of commercially available DMAs, a force is applied to a sample and the amplitude and phase of the resultant displacement are measured. These instruments utilize a linear actuator where the applied force is calculated from knowledge of the input signal to the electromagnetic coils in the driver. An alternative to the above is the use of a force transducer to measure the applied load, with the sample held between this transducer and the magnetic driver. These are the two types of arrangements that are found with the forced nonresonance technique. In each case, the sample is driven at a frequency below that of the test arrangement. Typically, the frequency range of instruments is from 0.001 to 1000 Hz. Any measurements below 0.01 Hz take too long for most analytical experiments, especially if the data are required as a function of temperature. Resonance often occurs at frequencies greater than 100 Hz, depending upon sample stiffness.

Figure 4.17 shows an example of a DMA output for polytetrafluoroethylene. Samples of PTFE were analyzed by DMA in shear mode at a length to thickness ratio of 4:1. Figure 4.17(a) shows the DMA output of stress versus time versus temperature, the results of which have been converted to Fig. 4.17(b) by the *time−temperature superimposition* technique.

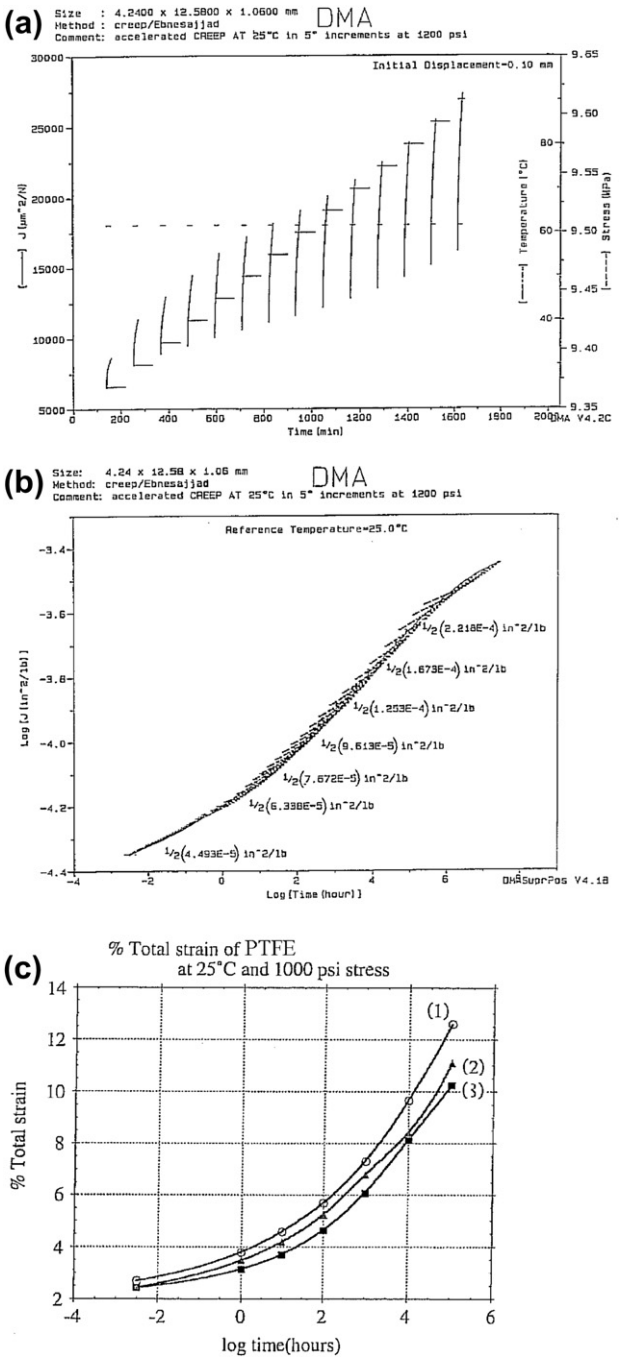

Figure 4.17 Examples of DMA graphs for three grades of PTFE.
(Courtesy DuPont Fluoroproducts.)

Time–temperature superimposition technique allows the prediction of material properties that normally would require measurements over many months or years. To collect the necessary data, measurement of a time-dependent variable is made at a number of temperatures. The curves are shifted mathematically along the time axis until some overlap occurs and a continuous curve is formed covering several decades of time; this curve is called the *master curve*. The master curve can be used to determine the time-dependent property as a function of time. Figure 4.17(c) shows total strain as a function of time and temperature for PTFE.

The choice of geometry will be dependent on the sample under investigation. For example, thin films can only be measured accurately in tension. High-quality dynamic mechanical testers perform well in tension and should apply the required pre-tension forces automatically, including those associated with large modulus changes that may occur at the glass transition. *Pre-tension* is necessary in order to maintain the sample under a net tension in order to prevent buckling that would otherwise occur. Tension should be the first choice for any sample less than 1 mm thick. Samples thicker than 1 mm will be likely too stiff for the instrument in tension; bending mode would be preferable in this case. Materials that creep excessively, such as polyethylene, may be difficult to test in tension, due to creep under the pre-tension force.

Readers interested in a more in-depth understanding of data obtained from DMA measurements can refer to polymer rheology textbooks. Helpful books on this topic include *Transport Phenomena* by Bird, Stewart, and Lightfoot, *Melt Rheology and its Role in Plastics Processing*—Theory and Applications, by J. M. Dealy and K. F. Wissbrun and *Polymer Melt Rheology*—A Guide for Industrial Practice, by F. N. Cogswell.[31,32]

4.18 Thermogravimetric Analysis (TGA)

TGA is a powerful technique for the measurement of thermal stability of materials including polymers. In this method, changes in the weight of a specimen are measured while its temperature is being increased. Moisture and volatile contents of a sample can be measured by TGA. The apparatus basically consists of a highly sensitive scale to measure weight changes and a programmable furnace to control the heat up rate of the sample. The balance is located above the furnace and is thermally isolated from the heat. A high precision hang-down wire is suspended from the balance down into the furnace. At the end of the hang-down wire is the sample pan, the position of which must be reproducible. The balance must be isolated from the thermal effects (e.g., by use of

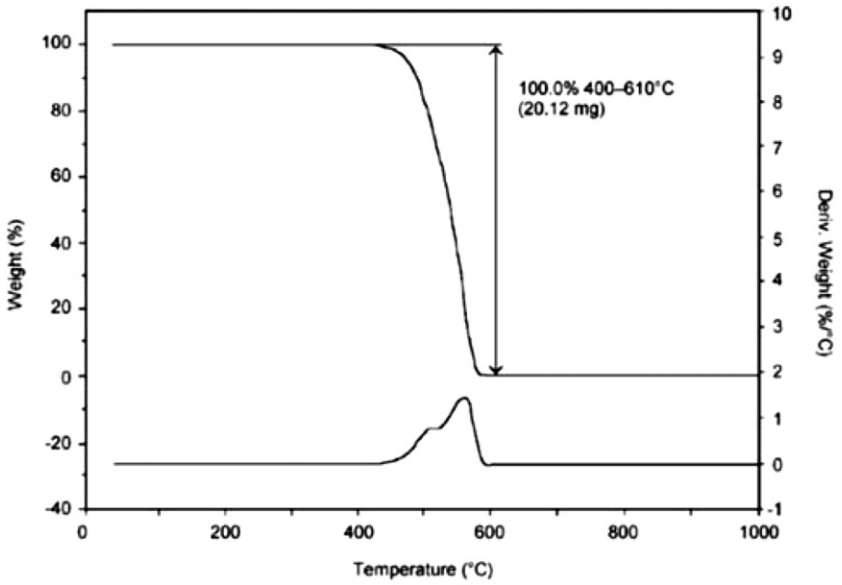

Figure 4.18 TGA thermogram of a neat FEP resin.
(Courtesy DuPont Fluoroproducts.)

a thermostatted chamber) to maximize the sensitivity, accuracy, and precision of weighing. Addition of an infrared spectrometer to TGA allows analysis and identification of gases generated by the degradation of the sample.

TGA apparatus is equipped with a microfurnace, which can be rapidly cooled. The heating element is made of platinum (reliable up to 1000 °C). An external furnace with a heating element made of an alloy of platinum and 30% rhodium can extend the temperature range to 1500 °C.

A modern apparatus is usually equipped with a computer that can calculate the weight-loss fraction or percentage. A commercial TGA is capable of >1000 °C, 0.1 μg balance sensitivity and a variable controlled heat-up rate under an atmosphere of air or another gas. Heat up rate capability of TGA may vary from 0.1 to 200 °C/min.

Figures 4.18 and 4.19 show the TGA spectra for the FEP resins, DSCs of which have been shown in the Figs 4.20 and 4.21. A comparison of these figures indicates deterioration in the thermal stability of FEP after incorporation of pigment. Figure 4.22 represents the TGA thermogram for a PTFE (31% wt.) compounded with carbon black (18% wt.) and silica (50.5% wt.). The 0.5% difference is due to the evolved volatile gases, which have not been shown in Fig. 4.22.

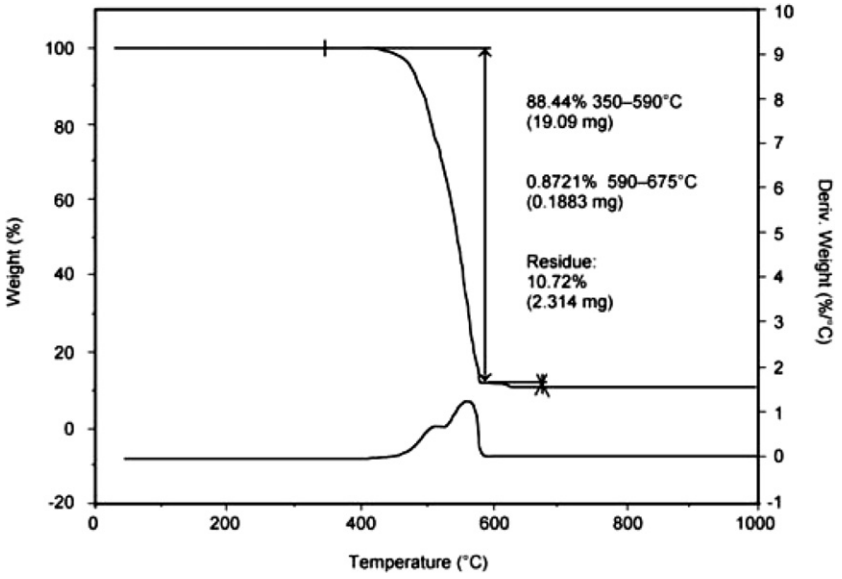

Figure 4.19 TGA thermogram of a pigmented FEP resin.
(Courtesy DuPont Fluoroproducts.)

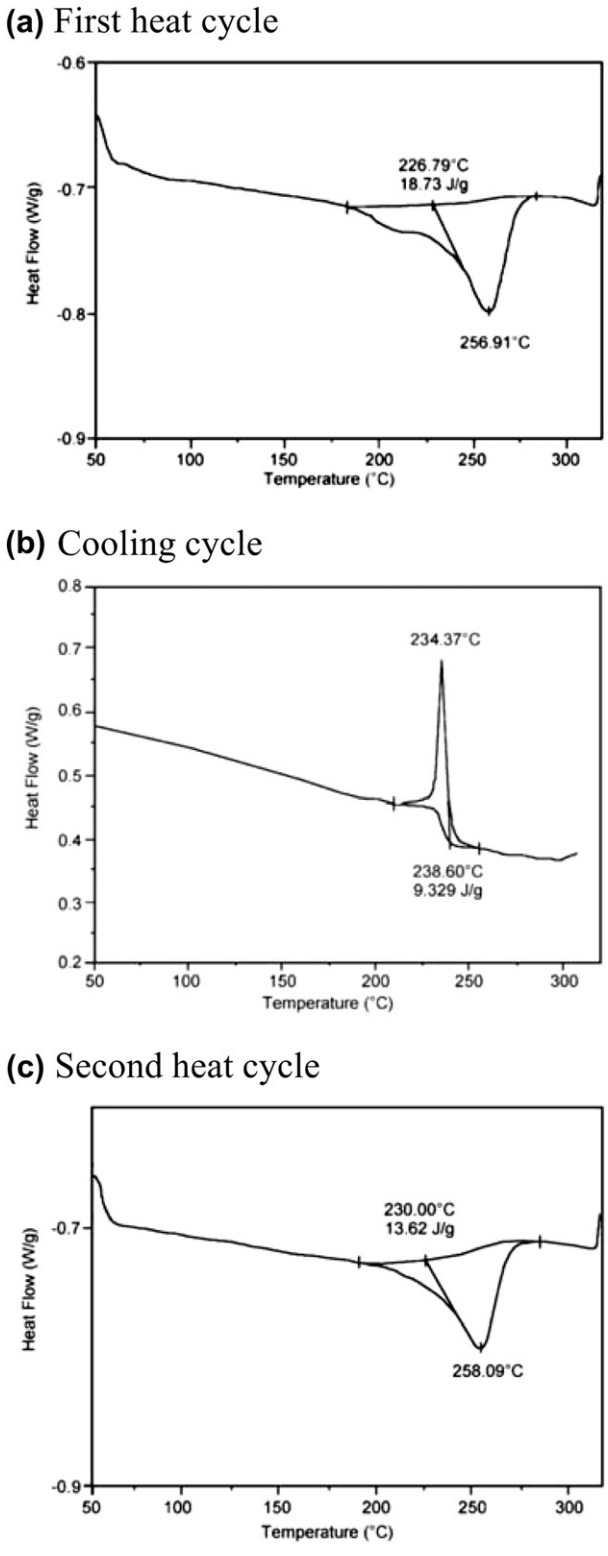

Figure 4.20 DSC thermograms of a neat FEP resin (melt flow rate = 30 g/10 min).
(Courtesy DuPont Fluoroproducts.)

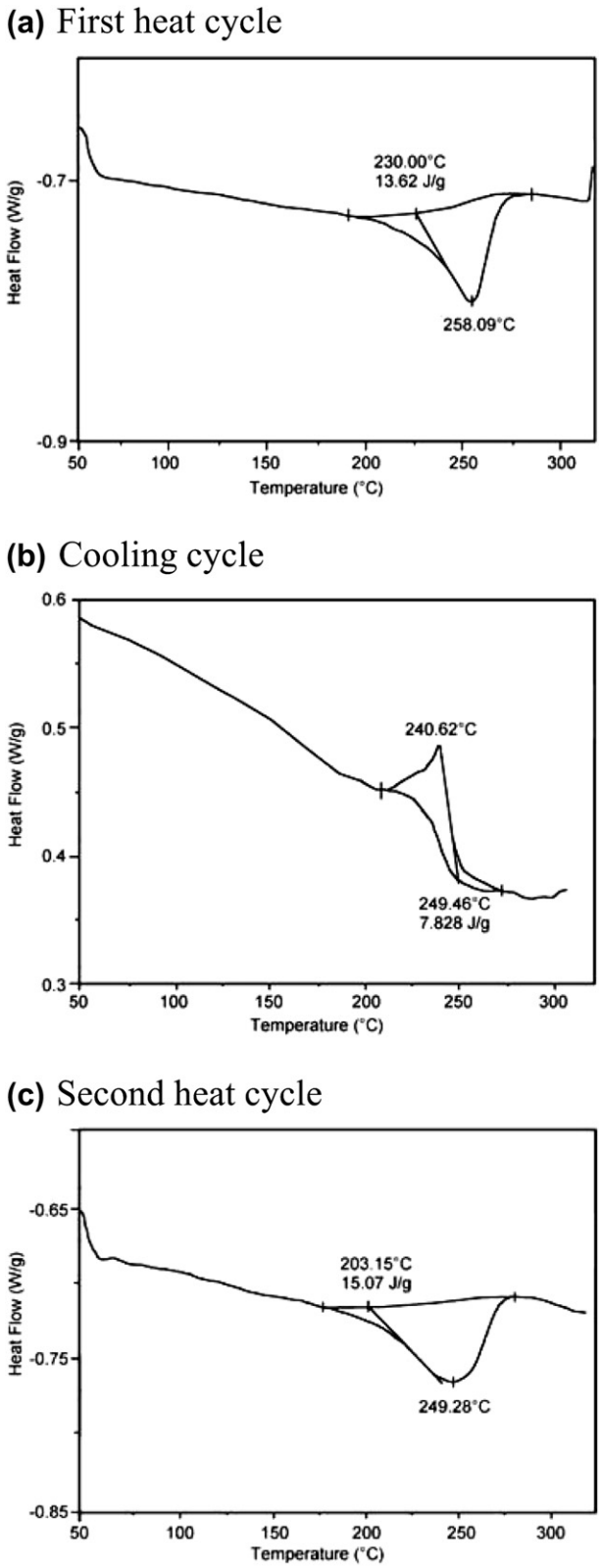

Figure 4.21 DSC thermograms of a pigmented FEP resin (melt flow rate = 30 g/10 min).
(Courtesy DuPont Fluoroproducts.)

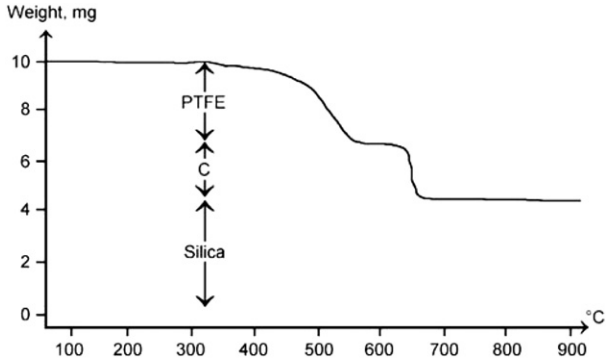

Figure 4.22 TGA thermograms of a pigmented PTFE resin.[35]
(Courtesy DuPont Fluoroproducts.)

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